



Formation of desert rose structures in vacuum plasma sprayed electrodes for alkaline electrolysis

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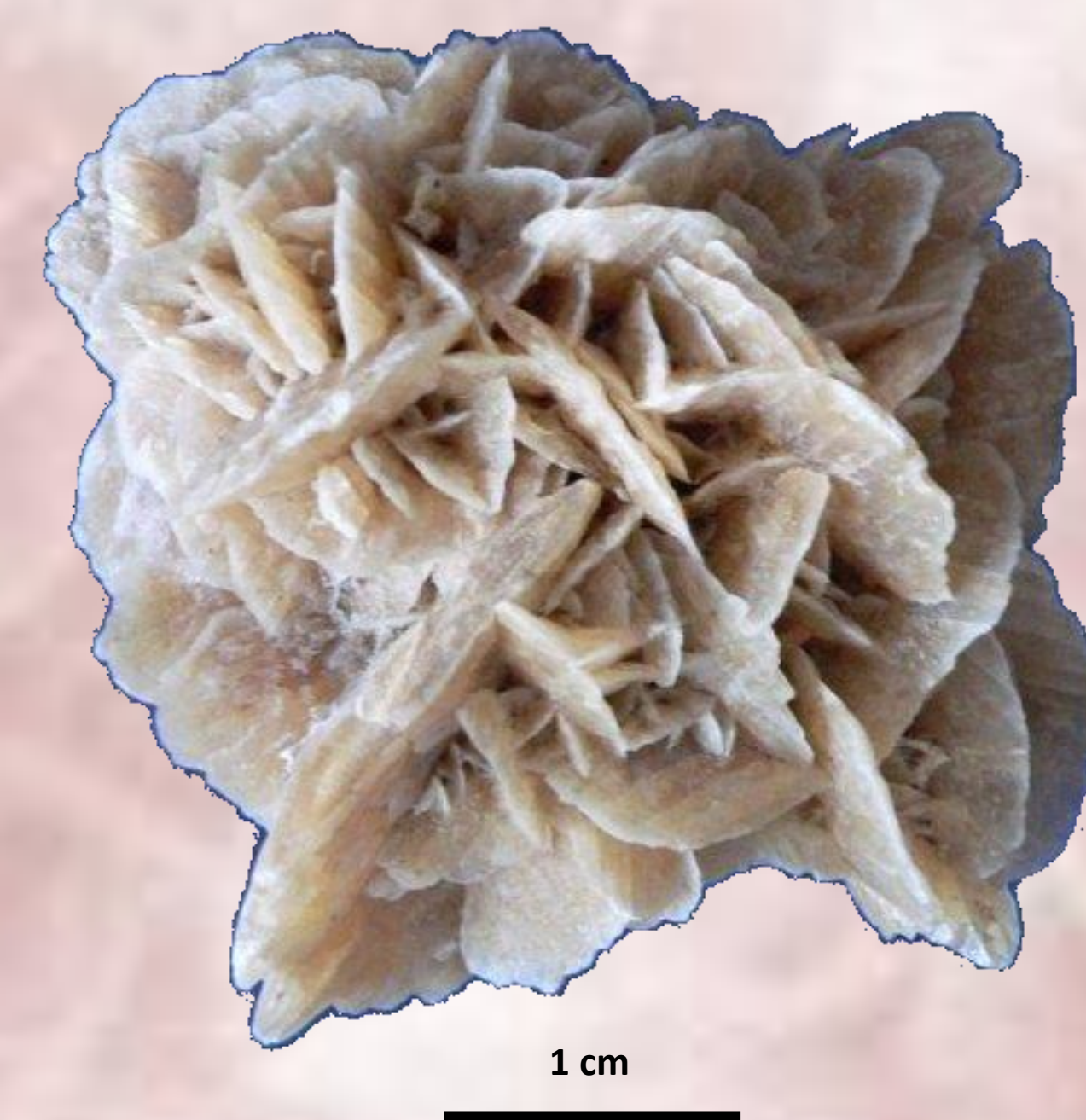
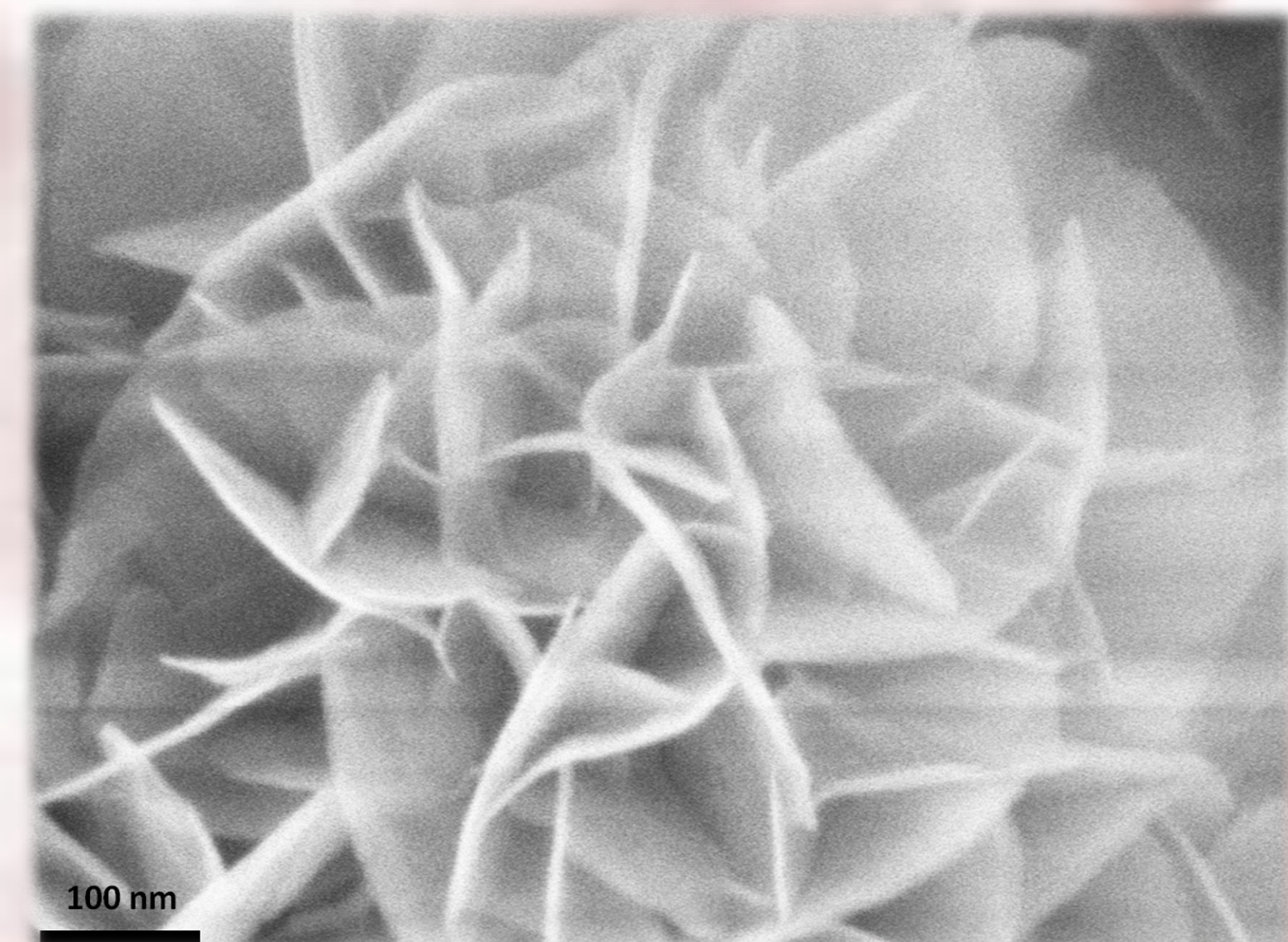
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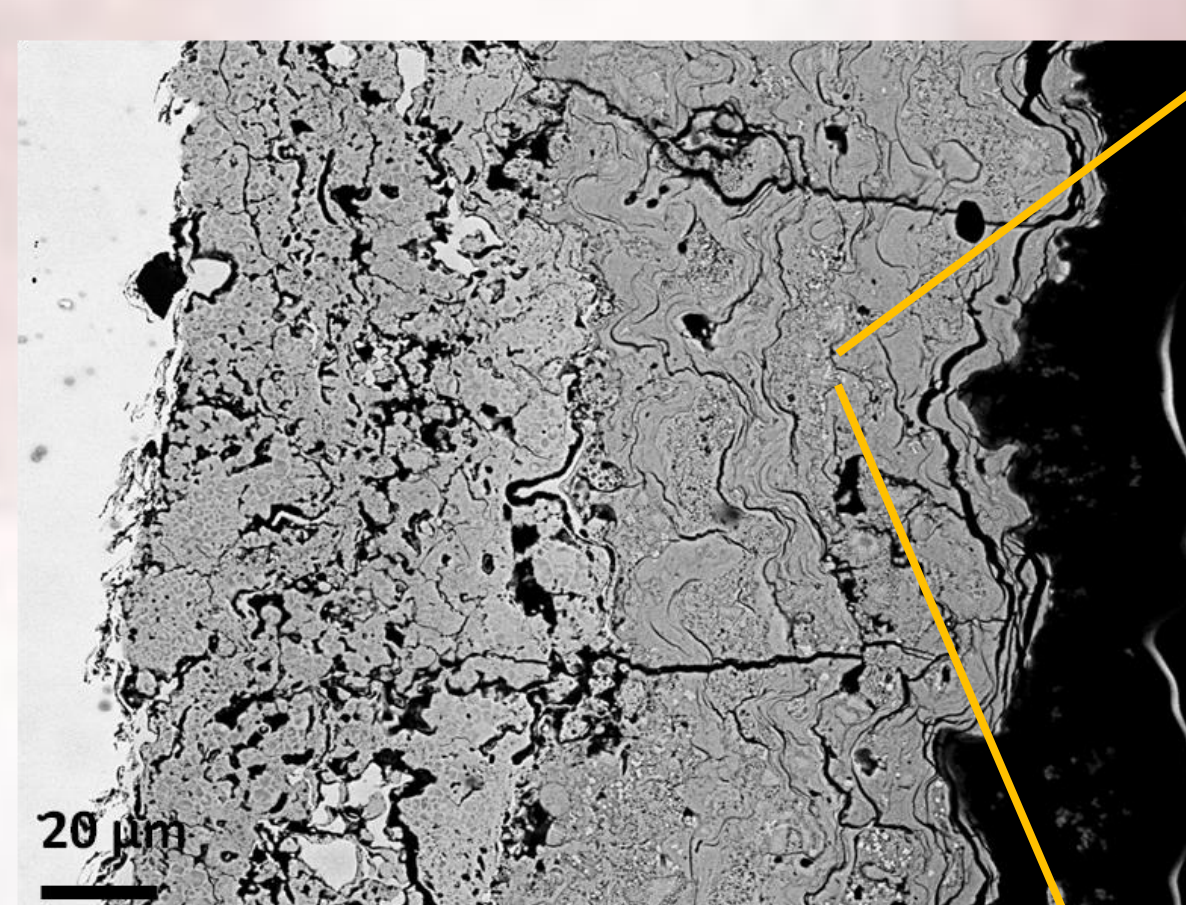
Introduction

The EU FCH-JU RESelyser project is concerned with the development of high pressure, high efficiency and low cost alkaline water electrolyzers that can be operated variably and intermittently to meet the demands for integration into energy networks relying on fluctuating renewable energy. The project utilizes NiAlMo alloy electrodes produced at the German Aerospace Center (DLR) by vacuum plasma spraying (VPS). VPS results in a heterogeneous microstructure consisting of a multitude of intermetallic phase sub domains and pores. Prior to electrolysis operation the electrodes are activated by leaching of Al and some Al containing intermetallic phases leaving micrometer pores and nanometer dendritic pores increasing the surface area available for the electrolysis reactions. Post mortem analysis of the electrodes revealed “desert rose” like nano flakes on the surfaces and in the pores. Earlier microscope analysis of Raney-Nickel electrodes for alkaline electrolysis (Ref. 1, 2, 3) has also reported on very fine unidentified nano structures on electrode surfaces. This study seeks to investigate the nature and the formation of these nano structures.

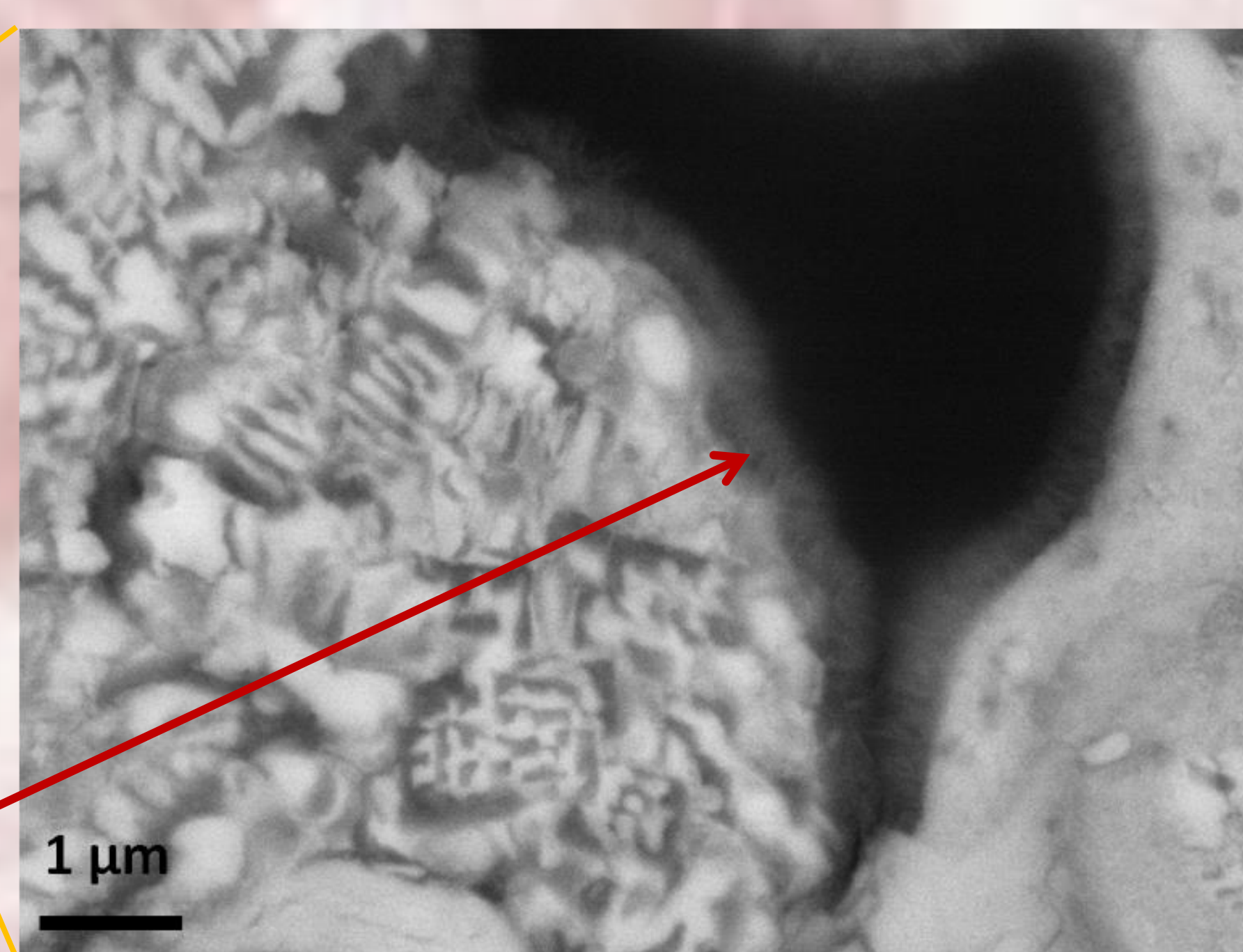


Results and discussion

Analyses of cross sections and electrode surfaces revealed desert rose like nano flake structures on the surfaces and in the pores of several electrodes, depending on the electrode history. The size of the faceted flakes varied from tens of nm to a couple of μm where the thickness varied from a few nm to ~ 20 nm. The particles were too fine for reliable EDS analysis in SEM. However, high oxygen and Al contents were indicated in the flakes. Similarly, the NiAlMo powder leached for Al showed emerging desert rose structure after storage in distilled water.

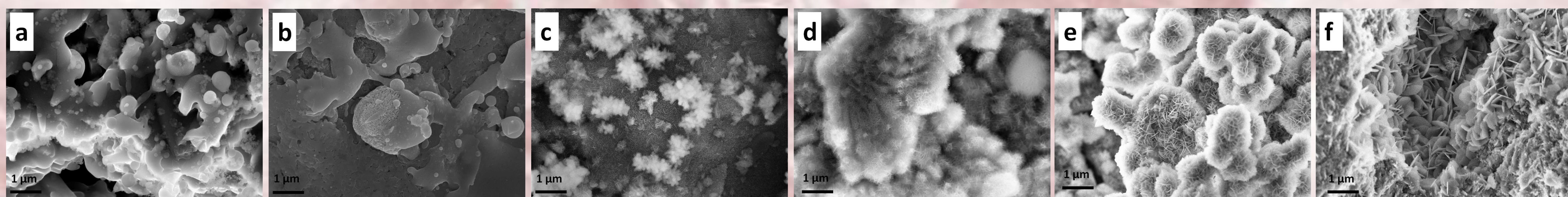


Cross section of NiAlMo electrode showing heterogeneous porous structure and nano particles on the pore surfaces.

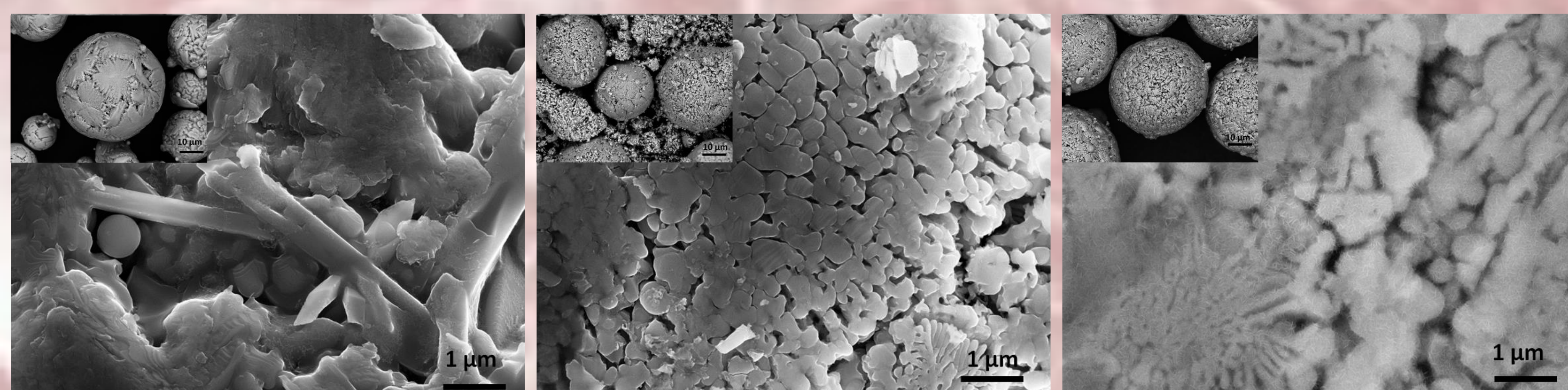


Experimental

Vacuum plasma sprayed NiAlMo alloy electrodes were characterized before and after electrolysis operation and after storage in distilled water for various length of time. For comparison, NiAlMo raw powder for VPS spraying, powder after leaching out Al, and the leached powder stored in distilled water for 40 days were also analyzed. The microstructural investigation was carried out applying a FEGSEM (Zeiss Supra 35) and HRTEM (JEM-3000F).

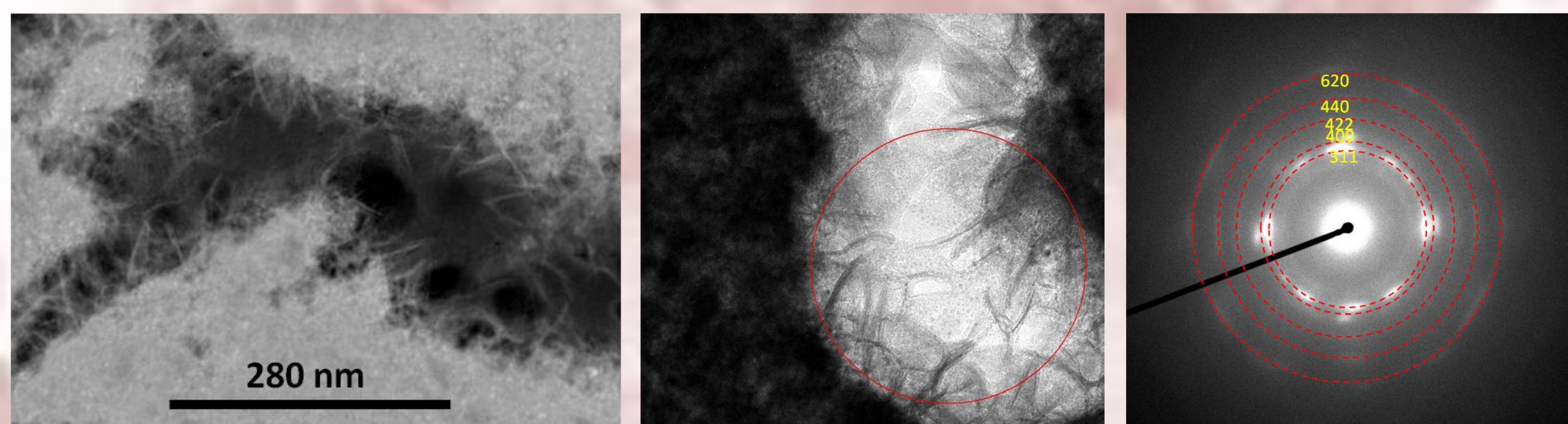


Formation of desert rose nano flakes on the NiAlMo electrode surfaces and in pores as a function of sample history. SEM images of electrode surfaces a) as sprayed; b) leached, washed and dried; c) leached, washed and stored in water 3 days; d) leached, washed and stored in water 210 days; e) leached, washed, stored 120 days in water, and operated as electrode for ~ 30 min.; f) leached, washed, stored 90 days in water, and operated as electrode for 28 days..



Formation of nano structures on the NiAlMo powders as a function of sample history. Left) NiAlMo raw powder; center) NiAlMo powder leached for Al; right) NiAlMo powder leached, washed and stored in distilled water for 40 days. Insets are powders in smaller magnification.

TEM on a lamella FIBed out of a NiAlMo electrode elucidated further on the desert rose structure. The main phases could be identified as Al_2NiO_4 ($a=b=c=8.046 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$) like phases and NiO by also considering the EDS results. Some other minor phases containing Fe and Mo may also exist. The study is still in progress.



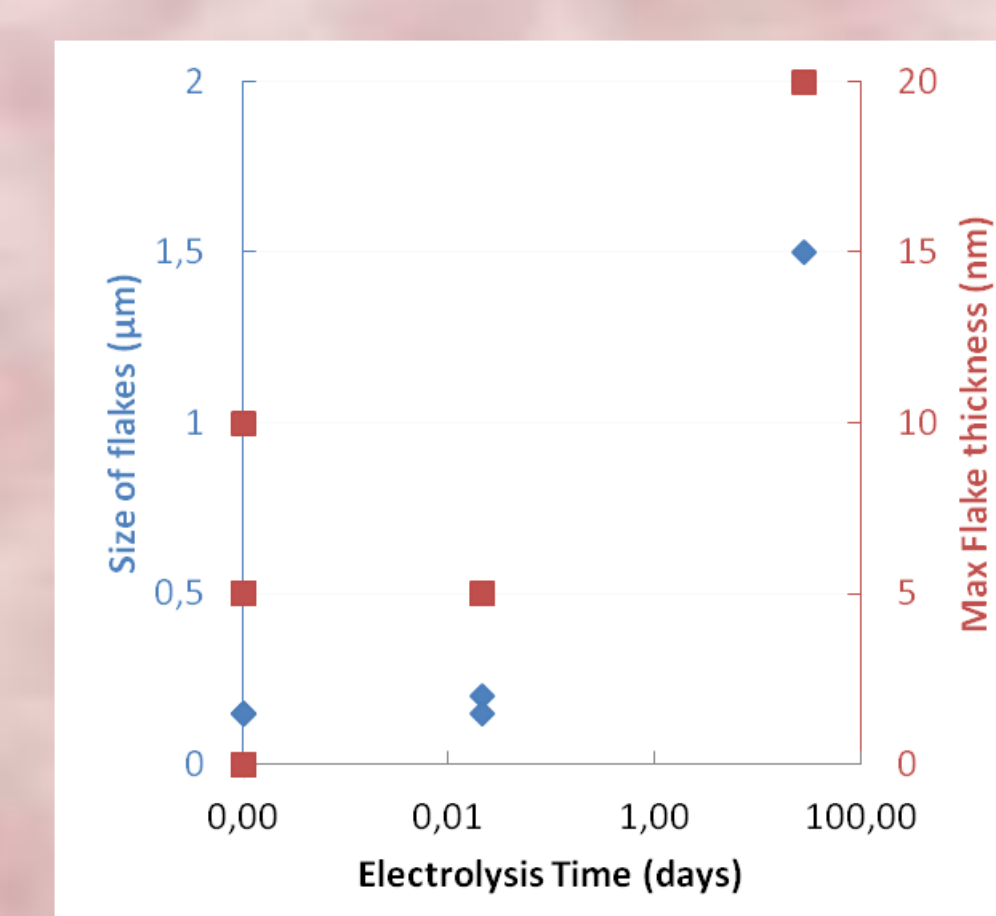
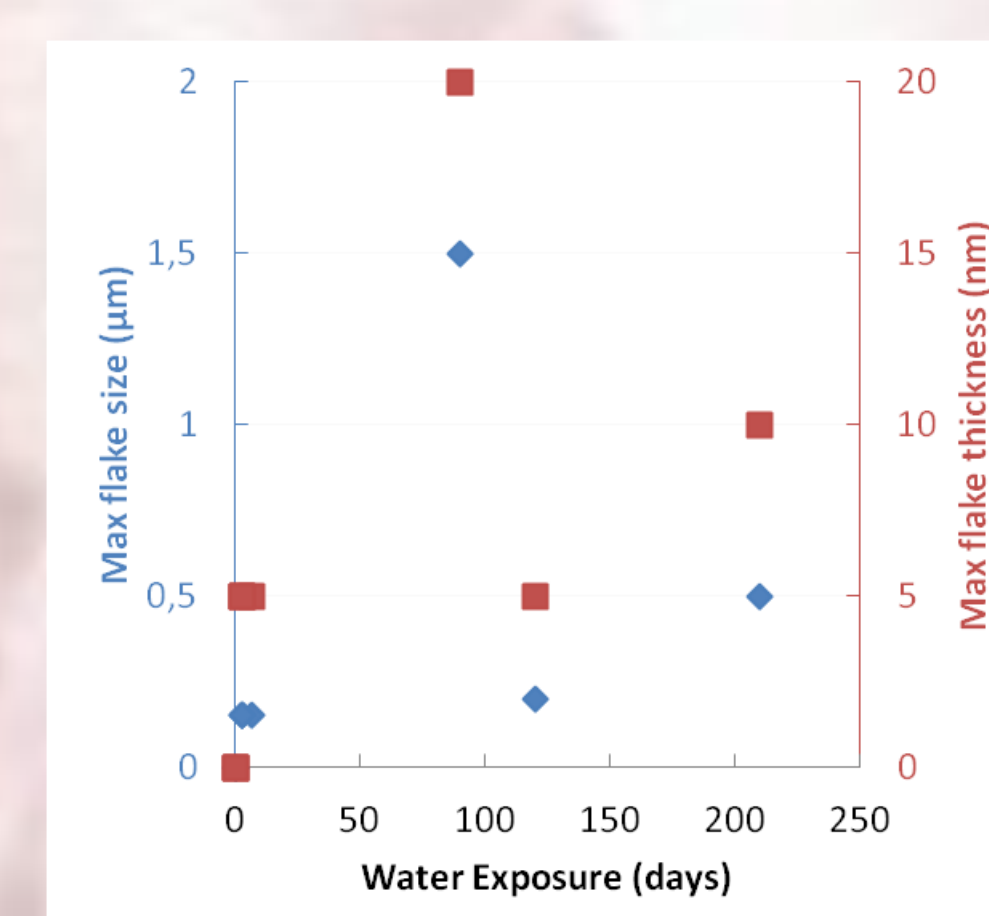
TEM images and diffraction patterns of areas with nano structures in the pores of a NiAlMo electrode after electrolysis.

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Evaluation of the flake size of the desert rose structure as function of sample history indicated that the formation of the desert rose structure was related to the electrolysis operation involving exposure to KOH and $\sim 70^\circ\text{C}$ as well as the duration of storage in distilled water at room temperature.



Flake size as a function of left) storage time in distilled water; right) electrolysis time.

Conclusion

The desert rose structure on the NiAlMo electrodes for alkaline electrolysis occurred only after storage in water and/or electrolysis operation; not on the “as VPS sprayed” or on the “by leaching Al activated” electrodes. The size of the flakes appeared to be more affected by the time of electrolysis/exposure to KOH at elevated temperature than by the time of storage in water. This data and our preliminary study of the chemical composition of the nano structured flakes lead us to suggest the following mechanism for the formation of the desert rose structure: Incomplete leaching of Al during activation of the electrodes can leave some Al that may dissolve in water and precipitate as oxidized species. In KOH at elevated temperature this could be more pronounced. The implications, positive or negative, for the application and performance of the electrodes would depend on the electronic and catalytic properties of the precipitates, and whether the precipitation takes place during operation or at breaks in the operation.

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